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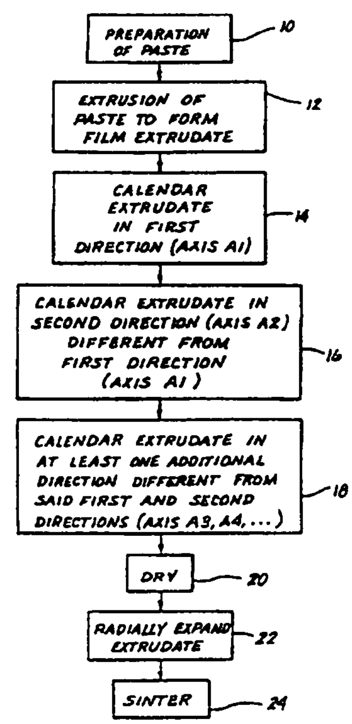
(54) Title: MULTIAXIALLY ORIENTED FLUOROPOLYMER FILMS AND METHODS OF MANUFACTURE THEREFOR

(57) Abstract

Porous fluoropolymer films, such as PTFE films, formed by a method comprising the steps of (a) forming a fluoropolymer (e.g., PTFE) paste (10), (b) extruding, calendaring, or otherwise processing the paste to form a film extrudate (12), (c) causing the film extrudate to be calendared in a first directional axis (14), (d) subsequently calendaring the film extrudate in a second directional axis which is different form the first directional axis (16), (e) subsequently calendaring the film extrudate in at least one additional direction axis which is different from said first and second directional axes, thereby forming a multiaxially calendared film extrudate (18), (f) drying the multiaxially calendared film extrudate (20), and (g) radially expanding the multiaxially calendared film extrudate (22) to form a radially oriented fluoropolymer (e.g., PTFE) film. The porous fluoropolymer films formed by this method are multiaxially oriented and exhibit isotropic strength properties.



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MULTIAXIALLY ORIENTED FLUOROPOLYMER FILMS AND METHODS OF MANUFACTURE THEREFOR

Field of the Invention

The present invention relates to porous fluoropolymer films, and more particularly to a multiaxially oriented, expanded, porous fluoropolymer film usable in biomedical patch graft applications.

Background of the Invention

Porous fluoropolymer films have been used in a wide variety of applications, including biomedical applications wherein fluoropolymer film patch grafts are surgically anastomosed into an existing organ or tissue for surgical repair or reconfiguration thereof. Synthetic patch grafts of this type are typically used to repair various anatomical structures and organs, including blood vessels, heart, skin, soft tissue, pericardium, etc.

One fluoropolymer commonly used for the manufacture of porous films is polytetrafluoroethelyne (hereinafter "PTFE"). PTFE has excellent heat resistance, chemical resistance, self-lubricity, non-adhesiveness and biological compatibility. As a result of these desirable properties, PTFE porous films have found wide applicability in medical, industrial and other applications.

A basic method for manufacturing porous PTFE films is described in U.S. Patent No. 4,478,665 (Gore). In accordance with this basic method, a PTFE paste is prepared by mixing crystalline PTFE fine powder with a quantity of liquid lubricant. The paste is subsequently extruded and calendared to form a wet, unsintered film extrudate. The film extrudate is cut into components. The components of PTFE containing a liquid lubricant are

placed in intimate contact. The film extrudate is subsequently dried, expanded in at least one axis, and sintered. The sintering process is carried out by heating the PTFE to a temperature above its crystalline melting point (327°C) but below the thermal degradation temperature thereof, for sufficient time to cause the PTFE polymer to substantially convert from its crystalline state to an amorphus state. In this regard, the sintering of PTFE is sometimes referred to as "amorphus locking" of the polymer.

Expanded, sintered PTFE films manufactured by the above-described basic process have a microstructure characterized by the existence of relatively dense areas known as "nodes" interconnected by elongate fibrils. The strength and porosity of the sintered PTFE film is largely a function of the directional orientation and spacing between the microstructural fibrils.

The directional orientation of the microstructural fibrils is determined by the directional axis or axes in which the film is a) calendared and b) expanded, prior to sintering thereof. Sintered PTFE films which have been calendared and expanded uniaxially typically have high strength only in the direction of the axis in which the film was calendared and expanded. Similarly, PTFE films which have been biaxially calendared and expanded may subsequently have high strength in both axes in which the film was previously calendared and expanded.

It is desirable to develop methods for manufacturing multiaxially calendared and expanded films which will exhibit substantially isotropic strength properties in all directions. Such multiaxially oriented films may exhibit highly uniform strength properties in all directions, thereby providing superior films for use in applications, such as biomedical patch graft applications, wherein multiaxial orientation and isotropic strength properties are desirable.

Prior efforts to manufacture multi axially oriented PTFE films have been described. For example, U.S. Patent No. 4,478,655 (Hubis) purports to describe a method for producing a composite or "multicomponent" porous PTFE film wherein a plurality of individual uniaxially oriented films are placed in juxtaposition, in varying orientations, and subsequently fused or laminated to one another to produce a composite article which exhibits composite multi axial orientation and isotropic strength properties.

There remains a need in the art for the development of new and/or improved methods for manufacturing thin, porous fluoropolymer films having multi axial fibril orientation and resultant isotropic strength properties after sintering.

Summary of the Invention

The present invention is a method of manufacturing expanded, porous, sintered, multi-axially oriented fluoropolymer film, said method comprising the steps of (a) forming a fluoropolymer (e.g., PTFE) paste, (b) extruding or otherwise processing the paste to form a film extrudate, (c) causing the film extrudate to be calendared in a first directional axis, (d) subsequently calendaring the film extrudate in a second directional axis which is different from the first directional axis, (e) subsequently calendaring the film extrudate in at least one additional directional axis which is different from said first and second directional axes, thereby forming a multiaxially calendared film extrudate, (f) drying the multiaxially calendared film extrudate, and (g) radially expanding the multiaxially calendared film extrudate to form a radially oriented fluoropolymer (e.g., PTFE) film.

Further in accordance with the invention, the repetitive calendaring steps (i.e., steps (c)-(e)) of the method may be accomplished using a single calendaring

machine, or a series of separate calendaring machin s, and th differing directional orientation of the workpiece may be accomplished by rotating or otherwise reorientating the film extrudate prior to each passage through the calendaring machine(s).

Still further in accordance with the invention, the drying of the multiaxially calendared film extrudate (i.e., step (f)) may be accomplished by heating the film extrudate to a temperature which is below the melting point of the fluoropolymer, but which is sufficiently high to cause evaporation of substantially all liquid lubricant contained in the film extrudate.

Still further in accordance with the invention, the step of radially expanding the multiaxially calendared film extrudate (i.e., step (g)) may be accomplished by any suitable radial expansion device or apparatus, including a panograft apparatus of the type described in United States Patent No. 3,953,566 (Gore).

Further objects and aspects of the invention may be apparent to those skilled in the art upon reading and understanding of the following detailed descriptions of the preferred embodiments, and upon consideration of the accompanying drawings.

Brief Description of the Drawings

Figure 1 is a block diagram showing a preferred method for manufacturing a multi axially oriented expanded fluoropolymer (e.g., PTFE) film in accordance with the present invention.

Figure 2 is a schematic diagram of one exemplary method for manufacturing multi axially oriented fluoropolymer film in accordance with the present invention.

Detailed Description of the Preferred Embodiments

The following detailed description and the accompanying drawings ar provided for purposes of

describing and illustrating presently preferred embodiments and examples of the invention only, and are not intended to limit the scope of the inv ntion in any way.

i. The Fluoropolymer Film Preparation Method of the Present Invention

Figure 1 shows a block diagram of the basic method of the present invention. The following paragraphs describe the individual steps of the basic method set forth in the block diagram of Figure 1.

Step A: Preparation of PTFE Paste

The initial step of the method is the preparation of an extrudable fluoropolymer paste 10.

Step B: Extrusion of Film

The fluoropolymer paste dispersion prepared in step 10 is subsequently extruded 12 to form a wet film extrudate. This is typically accomplished by passing the fluoropolymer paste dispersion through an extrusion machine at temperatures in the range of 18-50°C to form a wet film extrudate.

Step C: First Calendaring of Unsintered Film (AxisA_1)

The wet film extrudate is subjected to an initial calendaring step 14 wherein the extrudate is passed through at least one set of opposing stainless steel calendaring rollers which have an adjustable gap thickness therebetween. The gap thickness between the calendaring rollers is adjusted to decrease the thickness of the wet film extrudate as it passes between the calendaring rollers. Typically, the width of the unsintered film extrudate is maintained constant but the length thereof is allowed to increase as the thickness thereof decreases.

One example of a commercially available calendaring

machine useable for this step of the method is the small Killion two-roll stack (Killion Extruders, Inc., Ced r Grove, New Jersey 07009).

Step D: Second Calendaring in Second Direction (Axis A_2)

The unsintered film extrudate is subsequently subjected to a second calendaring step 16 wherein the film is calendared in a second direction (Axis A_2) which differs from the first direction (Axis A_1) in which the film was calendared during the initial calendaring step 14.

The completion of this second calendaring step 16 accomplishes biaxial orientation of the pre fibrillar regions of the film microstructure (i.e., the areas or regions which form the internodal fibrils upon expansion of the film) in the directions of axes A_1 & A_2.

This second calendaring step 16 may be carried out using the same type of calendaring device described hereabove with respect to the first calendaring step 14.

Step E: Third and Subsequent Calendaring (Axes $A_3 \ldots A_n$)

Following the second calendaring step 16, the unsintered film extrudate is subjected to at least one additional calendaring step 18 to cause the film to be further calendared in the direction of at least one additional axis (A_3, A_4, $A_5 \ldots$). The additional axis (A_3) or axes (A_3, A_4, ...) of prefibrilar orientation induced by this additional calendaring step(s) 18 differ(s) from the first and second axes A_1, A_2 of prefibrilar orientation induced during the first and second calendaring steps 14, 16. This results in a multiaxially oriented film extrudate.

This subsequent calendaring step(s) 18 may be carried out using the same type of calendaring device described hereabove with respect to the first and second calendaring steps 14, 16.

Step F: Drying of The Expanded Film Extrudate

The film extrudate is subjected to a drying step 20 wherein the liquid lubricant is removed from the film, thereby providing a dry film. This drying step 20 may be accomplished by heating the film in an oven or other suitable heating device to a temperature in the range of 100-300°C so as to cause rapid evaporation of the liquid lubricant from the matrix of the film. This drying step may be accomplished while the film remains clamped in a panograft device used to effect a subsequent radial expansion step 22 as described herebelow, or may be carried out with or without any other type of clamping or restraint on the film.

Step G: Radial Expansion of MultiAxially Calendared Extrudate

After completion of the drying step 20, the unsintered film extrudate is radially expanded 22.

This radial expansion step 22 may be carried out by affixing the multiaxially calendared film extrudate in a panograft device at 300°C of the type described in United States Patent No. 3,953,566 (Gore), and using such device to radially expand the film extrudate, preferably by an expansion ratio of 2:1-5:1.

Alternatively, this radial expansion step 22 may be carried out by blown extrusion technology whereby air or other gas is blown or forced against one side of the unsintered film extrudate while the periphery thereof is clamped or otherwise held in stationary position, thereby causing the desired radial expansion step 22.

Alternatively, this radial expansion step 22 may be carried out by clamping or otherwise holding the periphery of the film extrudate in a stationary position while advancing a pusher apparatus, such as an elongate rod having a rounded or blunt end, against the midregion of the film extrudate, thereby causing the desired radial expansion step 22 to be accomplished.

Step H: Sintering of the Radially Expanded Film Extrudate

Following drying and radial expansion of the film, the film is subjected to a sintering step 24. In this sintering step 24, the film is preferably restrained or compressed between two flat surfaces while being heated to a temperature above the melting point of the crystalline fluoropolymer but below the thermal degradation temperature thereof. Such heating and restraint of the film is maintained for a sufficient period of time to cause substantially complete sintering of the fluoropolymer.

By the above-described steps, the basic method of the present invention results in the formation of a multiaxially oriented, radially expanded fluoropolymer film having a preferred density of .3-1.0g/cm^3, and generally isotropic strength properties.

ii. Preparation of a Preferred Radially Stretchable PTFE Film by the Method of the Present Invention

Figure 2 is a step-wise illustration of an example whereby a radially oriented, PTFE film is manufactured by the method described hereabove and generally shown in the block diagram of Figure 1.

With reference to Figure 2, a quantity of PTFE paste 30 is prepared by blending unsintered PTFE fine powder having a crystallinity in excess of 90% (e.g., F103 or F104 Virgin PTFE Fine Powder, Dakin America, 20 Olympic Drive, Orangebury, New York, 10962) with a quantity of liquid lubricant such as odorless mineral spirits (e.g., Isopar®, Exxon Chemical Company, Houston, Texas 77253-3272) at a lubricant/powder weight ratio typically of about 25%. This PTFE paste 30 is of extrudable consistency and is passed through an extrusion die 32 to form an elongate extrudate 34. The extrudate 34 has a thickness T_1. The extrudate 34 is passed through a first calendaring device 36a (e.g., a small Killion Two Roll

Stack, Killion Extruders, Inc., Cedar Grove, New Jersey 07009), and is th r by calendared to form a film 38 having an initial thickness T_2. The extrudate 32 is initially passed through the first calendaring device 36a in the longitudinal direction of first axis A_1.

The film 38 of initial thickness T_2 is cut into a segment, such as a rectangle or square. The cut segment of film 38 is then rotated 90° and passed through a second calendaring device 36b in the direction of second axis A_2 perpendicular to the first axis A_1. As it passes through the second calendaring device 36b, the film 38 is calendared from its initial thickness T_2 to a decreased thickness T_3. Also, passage through the second calendaring device 36b results in biaxial orientation of the pre-fibrillar regions of the film 38. The width of the film 38 is maintained constant as it passes through the second calendaring device 36b, and the length of the film 38a is allowed to increase as the thickness decreases from T_2 to T_3. Thus, at this point in the process, the segment of film 38 has been calendared biaxially, in the directions of two perpendicular axes A_1 and A_2.

Thereafter, the segment of film 38 of thickness T_3 is rotated 45° and is passed through a third calendaring device 36c in the direction of third axis A_3. Third axis A_3 is, in the example shown, disposed at a 45° angle relative to axes A_1 and A_2, thereby accomplishing triaxial calendaring of the segment of film 38. As it passes through the third calendaring device 36c, the thickness of the segment of film 38 decreases from T_3 to T_4. Also, passage through the third calendaring device 36c results in triaxial orientation of the prefibrilar regions of the film 38. The width of the segment of film 38 is maintained constant as it passes through the third calendaring device 36c and the length thereof is permitted to increase as the thickness decreases from T_3 to T_4.

Thereafter, the segment of film 38 is again rotated 90° and passed, in the direction of a fourth longitudinal axis A_4, through a fourth calendaring device 36d. As it passes through the fourth calendaring device 36d the segment of film 38 decreases in thickness from T_4 to T_5. The width of the segment of film 38 is maintained constant as it passes through the fourth calendaring device 36d and the length thereof is permitted to increase as the thickness of the segment of film 38 decreases from T_4 to T_5. In the example shown, the fourth axis A_4 is at 90° to the third axis A_3, and at 45° to each of the first two axes A_1 and A_2. In this regard, after emerging from the fourth calendaring device 36d, the segment of film 38 has been quatriaxially calendared in the directions of four axes A_1-A_4. This results in corresponding quatriaxial orientation of the pre-fibrillar regions of the film 38.

Thereafter, the segment of film 38 is positioned on a flat surface and a circular center portion 38s is cut therefrom. The circular center portion 38s of the segment of film 38 is then affixed or clamped within a radial expansion device or panograft 40. Such radial expansion device or panograft 40 comprises a plurality of individual clamps 42 arranged in a circular configuration. The clamps 42 are connectable to the peripheral edge of the circular center portion 38s of the segment of film 38, as shown. Thereafter, while the film segment 38s remains clamped in the panograft device 40, but prior to any radial expansion thereof, the film segment 38s and panograft device 40 are positioned within drying device 44, such as the oven, wherein the temperature of the film is elevated to 100-300°C for a sufficient period of time to cause evaporation of the liquid lubricant therefrom.

The individual clamps 42 of the panograft device 40 are then concurrently moveable in outward, radially divergent directions while the temperature of the film

segment 38s is maintained at approximately 300°C so as to exert a radial expansion force on the circular portion 38s of film. This results in radial expansion of the circular portion 38s of film to form expanded film segment 38ex, as shown. The preferred ratio of radial expansion is in the range of 2:1 to 5:1. The radial expansion of the film 38, in conjunction with the preceding multiaxial calendaring thereof, results in multiaxial (i.e., radial) fibril orientation within the expanded film. One example of a radial expansion device or panograft 40 useable to effect this step of the process is that described in United States Patent No. 3,953,566 (Gore).

The dried, expanded film segment 38ex is then removed from the panograft device 40 and is subsequently compressed between two flat platens 46, as shown. The flat platens 46, along with the dried expanded film segment 38ex positioned therebetween, are then placed in a sintering device 48, such as an oven, and heated to a temperature above the crystalline melting point of PTFE (>327°C) but below the thermal degradation temperature of PTFE (e.g., <400°C) for a sufficient period of time to effect sintering of the PTFE.

Thereafter the sintered, expanded film segment 38ex is removed from between the platens 46 and is allowed to cool to room temperature.

The resultant expanded, sintered PTFE film segment 38ex has multiaxially oriented fibrils.

Those skilled in the art of manufacturing fluoropolymer films will appreciate that the foregoing detailed description may be subject to various additions, changes, deletions and/or alterations without departing from the intended spirit and scope of the invention. It is intended that all such additions, changes, deletions and/or alterations be included within the scope of the following claims.

WHAT IS CLAIMED IS:

1. A method of manufacturing multiaxially oriented fluoropolymer film, said method comprising the steps of:

a. providing a fluoropolymer paste;

b. forming the fluoropolymer paste into a film extrudate;

c. calendaring the film extrudate in a first directional axis;

d. calendaring the film extrudate in a second directional axis which is different from said first directional axis;

e. calendaring the film extrudate in at least one additional directional axis which is different from said first and second directional axes, thereby forming a multiaxially calendared film extrudate;

f. drying the multiaxially calendared film extrudate;

g. radially expanding the multiaxially calendared film extrudate to form a radially expanded film;

h. sintering the radially expanded fluoropolymer film.

2. The method of Claim 1 wherein step (a) comprises:

mixing a quantity of crystalline fluoropolymer powder with a quantity of liquid lubricant to form said fluoropolymer paste.

3. The method of Claim 1 wherein step (b) comprises:

extruding the fluoropolymer paste to form a film extrudate.

4. The method of Claim 1 where steps (b) and (c) are combined such that the fluoropolymer paste is formed into said film extrudate by initially calendaring the fluoropolymer paste in a first directional axis, thereby concurrently forming the fluoropolymer paste into a film extrudate and accomplishing the initial calendaring of

the film extrudate in the first directional axis.

5. The method of Claim 1 wherein said first and second directional axes are perpendicular to each other and wherein said at least one additional directional axis comprises third and fourth directional axes, each of said third and fourth directional axes being at an angle of approximately 45 degrees relative to one of said first and second directional axes.

6. The method of Claim 1 wherein said fluoropolymer is PTFE.

7. The method of Claim 1 wherein step (b) comprises:

advancing said film extrudate in the direction of the first directional axis, in contact with at least one calendaring roller, such that said calendaring roller will cause the advancing film extrudate to decrease in thickness.

8. The method of Claim 1 wherein step (d) comprises:

reorienting the film extrudate following completion of the first calendaring of step (c), and subsequently advancing the reoriented film extrudate in the direction of the second directional axis, in contact with at least one calendaring roller, such that said calendaring roller will cause the advancing film extrudate to further decrease in thickness.

9. The method of Claim 1 wherein step (e) comprises:

reorienting the film extrudate following the second calendaring of step (d) and subsequently advancing the reoriented film extrudate in the direction of the third directional axis, in contact with at least one calendaring roller, such that said calendaring roller will cause the advancing film extrudate to further decrease in thickness.

10. The method of Claim 9 wherein step (e) further comprises:

subsequently reorienting the film extrudate following the third calendaring step of step (e) and subsequently advancing the film extrudate in the direction of a fourth directional axis, in contact with at least one calendaring roller, such that said calendaring roller will cause further reduction in the thickness of the advancing film.

11. The method of Claim 1 wherein step (f) comprises:

heating the film to a temperature which causes evaporation of any liquid lubricant contained within the film.

12. The method of Claim 1 wherein step (g) comprises:

cutting a substantially round segment of the multiaxially calendared film extrudate, said substantially round segment having a substantially round peripheral edge;

attaching a plurality of clamping apparatus about the peripheral edge of said substantially round segment of film extrudate; and

causing said clamping apparatus to concurrently move in radially outward directions to thereby effect radial expansion of said substantially round segment of film extrudate.

13. The method of Claim 12 wherein said clamping apparatus are incorporated into a panograft device.

14. The method of Claim 1 wherein the radial expansion of step (g) is carried out at an expansion ratio in the range of 2:1 - 10:1.

15. The method of Claim 1 wherein step (h) comprises:

heating the radially expanded fluoropolymer film to a temperature above the crystalline melting point of the fluoropolymer but below the thermal

degradation temperature of the fluoropolymer for a sufficient period of time to cause sintering of the fluoropolymer.

16. The method of Claim 1 wherein the fluoropolymer is PTFE and wherein step (h) comprises heating said PTFE film to a temperature between 327°C and 400°C for a sufficient period of time to cause sintering of the PTFE.

17. The method of Claim 1 wherein step (g) comprises:

radially expanding the multiaxially calendared film extrudate by blown extrusion whereby pressurized gas is blown against the film extrudate to cause radial expansion thereof.

18. The method of Claim 1 wherein the multiaxially calendared film extrudate at step (g) has a middle region and a periphery, and wherein the radial expansion of step (g) comprises:

advancing a blunt-ended pusher device against the midregion of said multiaxially calendared film extrudate while holding the periphery thereof in stationary position, thereby causing radial expansion of the multiaxially calendared film extrudate.

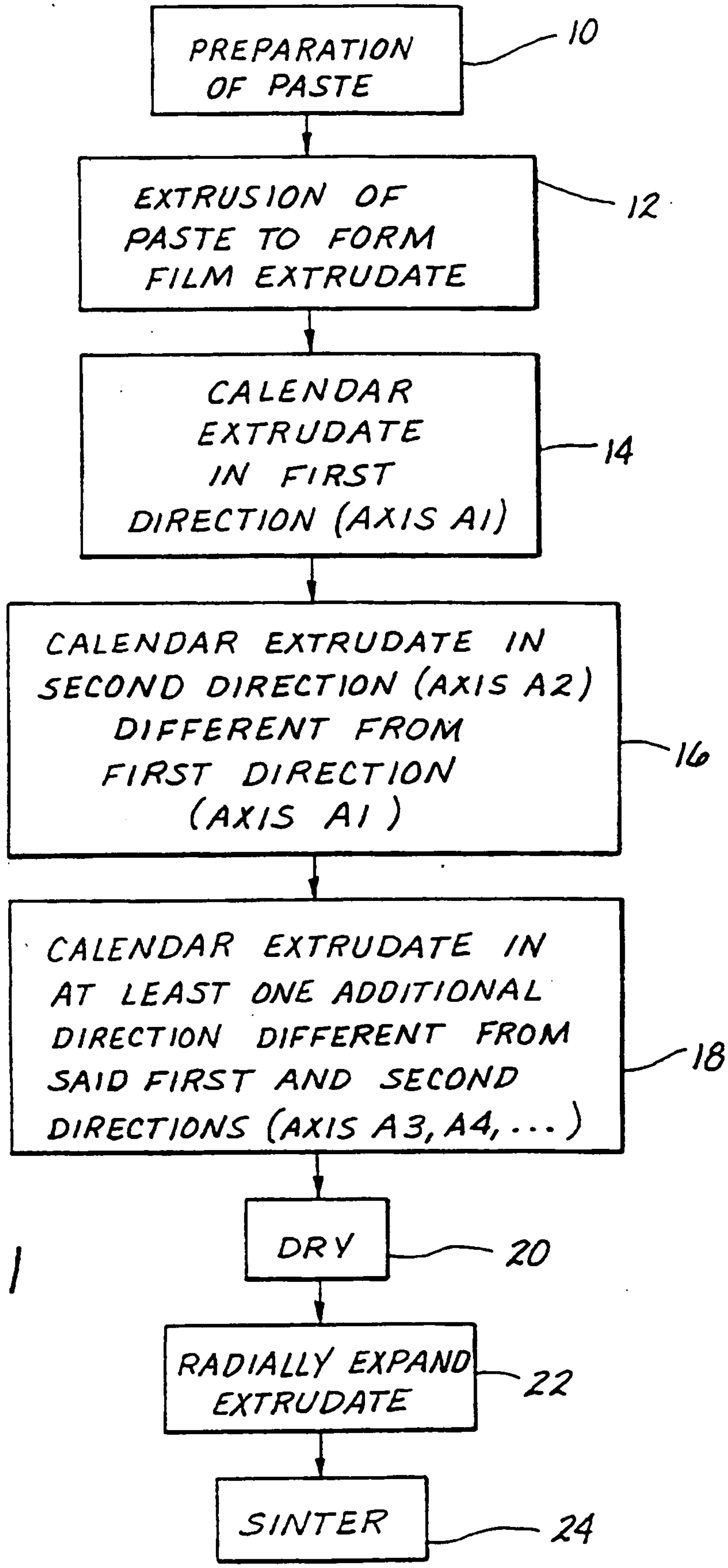
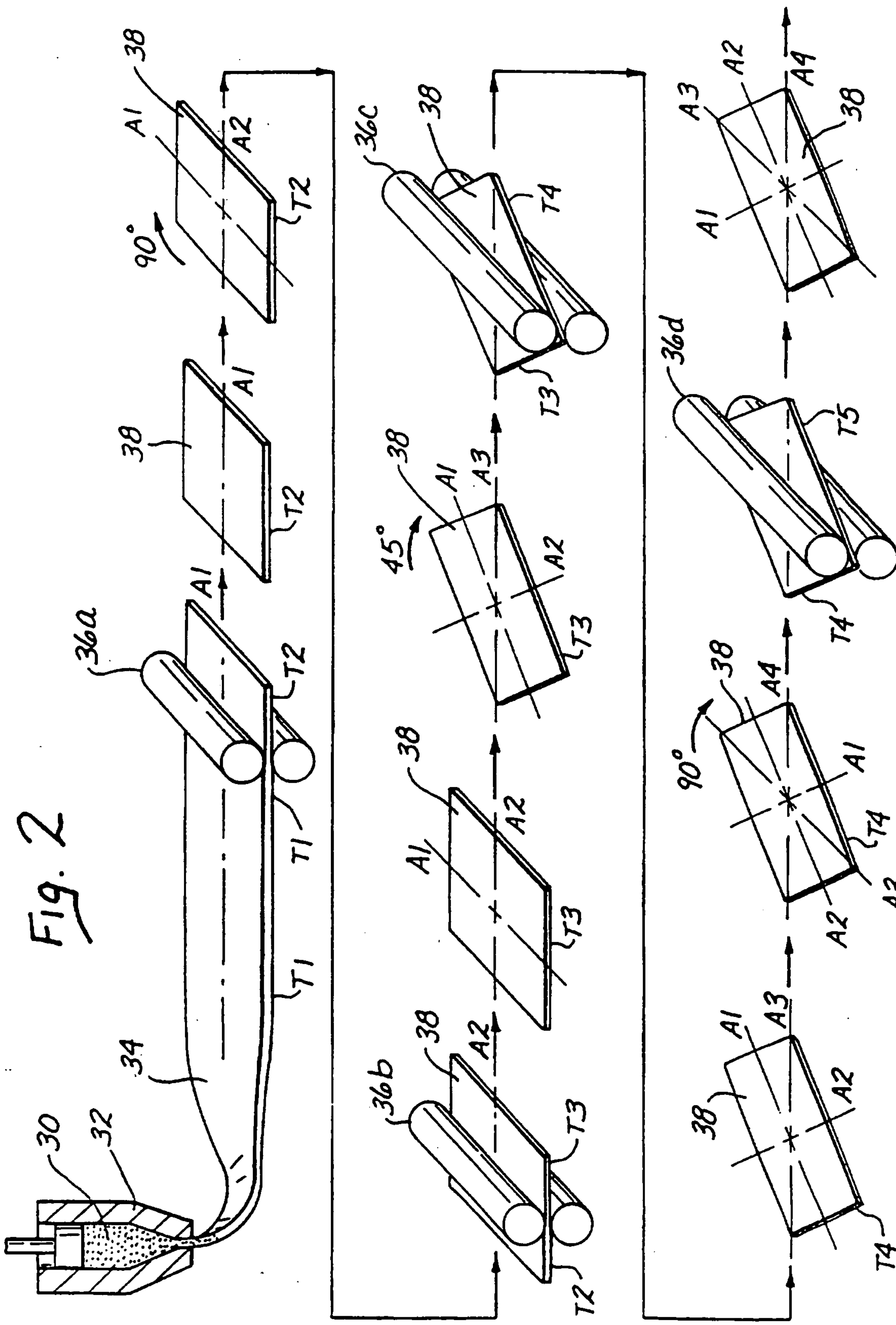

PREPARATION OF PASTE
10
EXTRUSION OF PASTE TO FORM FILM EXTRUDATE
12
CALENDAR EXTRUDATE IN FIRST DIRECTION (AXIS A1)
14
CALENDAR EXTRUDATE IN SECOND DIRECTION (AXIS A2) DIFFERENT FROM FIRST DIRECTION (AXIS A1)
16
CALENDAR EXTRUDATE IN AT LEAST ONE ADDITIONAL DIRECTION DIFFERENT FROM SAID FIRST AND SECOND DIRECTIONS (AXIS A3, A4, ...)
18
DRY
20
RADIALLY EXPAND EXTRUDATE
22
SINTER
24

Fig. 1

Fig. 2



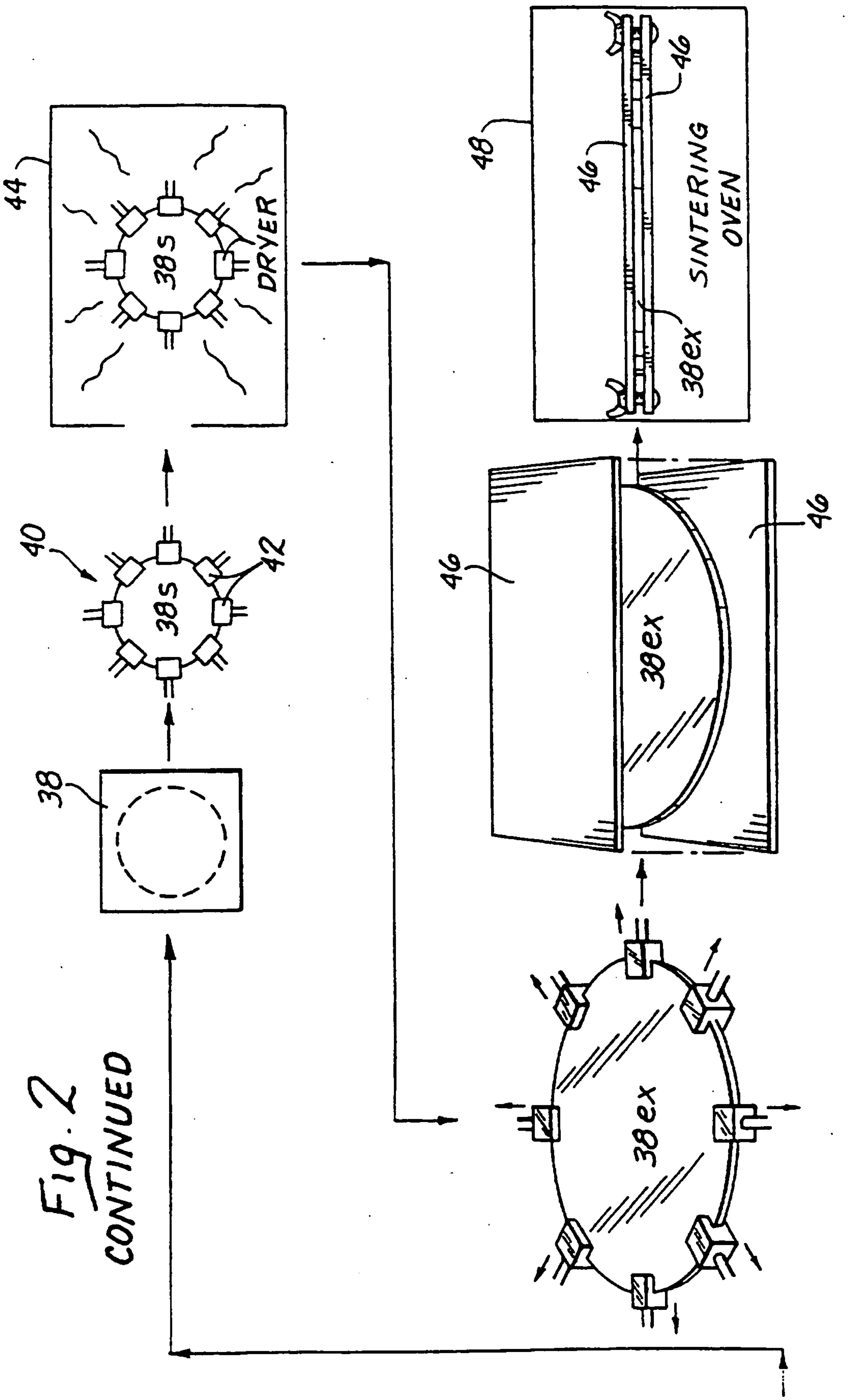


Fig. 2 CONTINUED

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/03251

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B29C55/18 B29C55/10 //B29K27:18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 321 109 A (BOSSE CHARLES F ET AL) 14 June 1994 see column 10, line 6 - column 11, line 59; figures 10-12 ---	1-18
A	GB 1 104 139 A (DU PONT) 21 February 1968 see claim 7 ---	1-18
A	DE 14 94 293 A (DU PONT) 30 January 1969 see example 2 ---	1-18
A	US 2 952 867 A (DIEDRICH ET AL.) 20 September 1960 see column 2, line 48 - line 63 ---	17
A	US 4 128 383 A (BOND THOMAS J ET AL) 5 December 1978 see figure 2 ---	18

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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1

Date of the actual completion of the international search	Date of mailing of the international search report
9 June 1997	01.07.97
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